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(54) DIELECTRIC PORCELAIN COMPOSITION AND MANUFACTURE THEREOF

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## (57)Abstract:

PURPOSE: To significantly reduce change in the dielectric constant of a lead- combined perovskite dielectric material due to temperature without significantly lowering the dielectric constant.

CONSTITUTION: In a lead-combined perovskite dielectric porcelain composition,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3\text{--Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ ,  $\text{WO}_3$  is added by 1 to 10 parts by weight as additive to the main composition with the ranges of composition points as follows: A=(50, 30, 20), B=(40, 40, 20), C=(30, 40, 30), D=(30, 30, 40), E=(40, 20, 40) and F=(50, 20, 30). A core-shell structure of W and Nb is formed within the perovskite crystal grain.

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(54)【発明の名称】 誘電体磁器組成物及びその製造方法

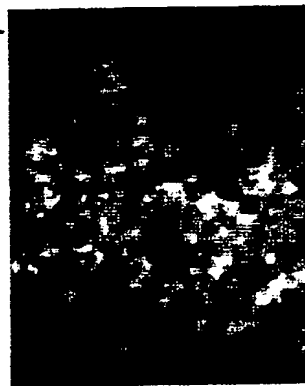
## (57)【要約】

【目的】 鉛複合ペロブスカイト系誘電体材料の誘電率を著しく低下させることなく、温度による誘電率の変化を著しく小さく抑える。

【構成】 鉛複合ペロブスカイト系誘電体磁器組成物であって、 $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3-Pb(Mg_{1/2}W_{1/2})O_3$ において、以下の組成点  $A=(50, 30, 20)$ 、 $B=(40, 40, 20)$ 、 $C=(30, 40, 30)$ 、 $D=(30, 30, 40)$ 、 $E=(40, 20, 40)$ 、 $F=(50, 20, 30)$ 、で表される範囲内の主組成に、添加物として $WO_3$ を主組成に対して1~10重量部添加して、ペロブスカイト結晶粒内にWとNbのコア-シェル構造を形成させた組成物。

図面代用写真

図2



写真

図2 ペロブスカイト結晶粒のコア-シェル構造を  
しめす走査電顕写真 ( $WO_3 = 5\%$ 添加組成)

## 【特許請求の範囲】

【請求項1】 マグネシウムニオブ酸鉛、チタン酸鉛、マグネシウムタングステン酸鉛からなる組成物〔 $Pb(Mg_{1/3}Nb_{2/3})O_3$ 、 $PbTiO_3$ 、 $Pb(Mg_{1/2}W_{1/2})O_3$ 〕において、以下の組成点A=(50, 30, 20)、B=(40, 40, 20)、C=(30, 40, 30)、D=(30, 30, 40)、E=(40, 20, 40)、F=(50, 20, 30)、で表される六角形の内部または線上の範囲の主組成に、添加物として $WO_3$ を主組成に対して1~10重量部添加したことを特徴とする誘電体磁器組成物。

【請求項2】 前記誘電体磁器組成物の結晶粒径が0.5  $\mu m$ 以上、10  $\mu m$ 以下である請求項1に記載の誘電体磁器組成物。

【請求項3】 誘電体磁器組成物の製造方法において、材料成分がマグネシウムニオブ酸鉛、チタン酸鉛、マグネシウムタングステン酸鉛からなる組成物〔 $Pb(Mg_{1/3}Nb_{2/3})O_3$ 、 $PbTiO_3$ 、 $Pb(Mg_{1/2}W_{1/2})O_3$ 〕において、以下の組成点A=(50, 30, 20)、B=(40, 40, 20)、C=(30, 40, 30)、D=(30, 30, 40)、E=(40, 20, 40)、F=(50, 20, 30)、で表される六角形の内部または線上の範囲の主組成に、添加物として $WO_3$ を主組成に対して1~10重量部添加した組成からなり、当該材料成分を、所望の組合せで混合、粉碎、成形、および焼成する各工程を含み、且つ、前記焼成工程を1100℃~1200℃の温度範囲で行うことを特徴とする誘電体磁器組成物の製造方法。

【請求項4】 前記材料成分のうち複合ペロブスカイトのBサイト成分(Mg, Nb, Ti, W)の一種以上の元素を含む材料成分を、混合し、熱処理して、複合酸化物を予め生成し、その後他の材料成分を加えて所望の最終組成とすることを特徴とする請求項3に記載の誘電体磁器組成物の製造方法。

【請求項5】 鉛系複合ペロブスカイトを主成分とする磁器組成物において、ペロブスカイト結晶粒内の芯部と側部との間に構成元素WとNbの不均一分布を伴う誘電体磁器組成物。

【請求項6】 鉛系複合ペロブスカイトを主成分とする磁器組成物において、ペロブスカイト結晶粒内の芯部と側部との間に構成元素の不均一分布があり、最大濃度と最小濃度の差が最大濃度の20%以上である誘電体磁器組成物。

【請求項7】 前記ペロブスカイト結晶粒の結晶粒径が0.5  $\mu m$ 以上、10  $\mu m$ 以下である請求項5または請求項6に記載の誘電体磁器組成物。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は積層セラミックコンデンサなどに用いる誘電体磁器組成物に関し、特に誘電率が

大きく、温度依存性が少なく、低温焼成が可能で、粒径の細かい誘電体磁器組成物に関する。

## 【0002】

【従来の技術】 積層セラミックコンデンサに用いられる誘電体として、従来チタン酸バリウム系誘電体が用いられてきた。この誘電体は添加物等と組み合わせることによってJISのF特性相当(温度範囲-25~+85℃で容量偏差+30, -80%以内)で誘電率15000程度、X7R特性相当(温度範囲-55~+125℃で容量偏差が±15%以内)で誘電率5000程度を有する等の優れた特性を示し、セラミックコンデンサの誘電体としてひろく用いられてきている。

【0003】 一方、近年、素子としての小型化高容量の要求にもとずき積層セラミックコンデンサの一層あたりの誘電体厚みが数ミクロン程度にまで薄層化が進んできた。

【0004】 チタン酸バリウム系素材の場合印加される電界が強いほど誘電率が低下する特徴を合わせ持ち、素子の小型高容量化の要求が高まるにつれて対応がむずかしくなっている。

【0005】 チタン酸バリウム系素材のほかに鉛系複合ペロブスカイト系素材が高誘電率系素材として知られている。この材料はJISのF特性相当で誘電率25000程度を示し興味ある材料として実用化の検討がひろく行われてきている。但しこの材料は、機械的強度がとれない、鉛の揮発等が問題となり焼成が難しい、めっき液によって絶縁劣化をおこしやすいなど問題点の多い材料でもある。

【0006】 しかしながら、高誘電率を有すること、また、一般に1000℃から1200℃程度で焼成できることなどの利点があげられ、積層セラミックコンデンサの内部電極を従来のパラジウム100%からパラジウム-銀合金、銀100%で置き換えることができるため、高誘電率で内部電極を多く必要とする1  $\mu F$ 以上の比較的高容量の素子で実用化されてきた。

【0007】 また、一般に鉛系複合ペロブスカイト系素材はバイアス電界による誘電率の減少が小さくチタン酸バリウム系素材に比べて約半分程度である。上述したような小型高容量化への要求に対応する材料としても鉛系複合ペロブスカイト系材料が注目されてきている。

【0008】 チタン酸バリウムは逐次相転移を示し、-10℃付近と+120℃付近で相転移が起き、これに対応して誘電率のピークもこの温度付近で2回極大値を持つ。

【0009】 これに適当に添加物、また、コアシェル構造等の組成不均一構造を組み合わせることによって、X7R特性、B特性(温度範囲-25~+85℃で容量偏差が±10%以内)などの温度依存性の少ない材料で誘電率5000程度の特性を示している。

【0010】 一方、鉛系複合ペロブスカイト系材料の場合

合、一般に逐次相転移を示さず、誘電率のピークも1回の極大値を示すだけである為、チタン酸バリウム系素材と違って、X7R特性、B特性で高誘電率の特性を示すのは困難と考えられていた。

【0011】尚、コアシェル構造については、日本セラミックス協会1991年会講演予講集2C34, pp266、日本電子工業会新機能複合電子材料研究会平成3年度第4回研究会資料2に報告があるがX7RまたはB特性を満たすほどの温度特性の平坦化は行われてなく、また、誘電率についての記載も見られない。

【0012】このような状況から鉛系複合ペロブスカイト系誘電体についてこの材料の利点と、誘電率の温度特性が平坦で誘電率の大きいことを合わせ持つ磁器組成物が求められている。

【0013】

【発明が解決しようとする課題】 $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3 - Pb(Mg_{1/2}W_{1/2})O_3$  鉛系複合ペロブスカイト系素材を用い温度変化率の少ない誘電体磁器組成物を得ようとする場合、一般に誘電率が2000~3000程度まで減少するという問題があった。

【0014】本発明は $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3 - Pb(Mg_{1/2}W_{1/2})O_3$  鉛系複合ペロブスカイト系素材を用いて誘電率を著しくそこなうことなく、温度変化率の少ない、合わせて鉛系複合ペロブスカイト系素材の利点を持つ誘電体磁器組成物を提供することを目的としている。

【0015】

【課題を解決するための手段】即ち、本発明は、マグネシウムニオブ酸鉛、チタン酸鉛、マグネシウムタングステン酸鉛からなる組成物 $[Pb(Mg_{1/3}Nb_{2/3})O_3, PbTiO_3, Pb(Mg_{1/2}W_{1/2})O_3]$ において、以下の組成点A=(50, 30, 20)、B=(40, 40, 20)、C=(30, 40, 30)、D=(30, 30, 40)、E=(40, 20, 40)、F=(50, 20, 30)、で表される六角形の内部または線上の範囲の主組成に、添加物として $WO_3$ を主組成に対して1~10重量部添加したことを特徴とする誘電体磁器組成物である。

【0016】また、好ましくは、前記誘電体磁器組成物の結晶粒径が $0.5\mu m$ 以上、 $10\mu m$ 以下である誘電体磁器組成物である。

【0017】また本発明は、誘電体磁器組成物の製造方法において、材料成分がマグネシウムニオブ酸鉛、チタン酸鉛、マグネシウムタングステン酸鉛からなる組成物 $[Pb(Mg_{1/3}Nb_{2/3})O_3, PbTiO_3, Pb(Mg_{1/2}W_{1/2})O_3]$ において、以下の組成点A=(50, 30, 20)、B=(40, 40, 20)、C=(30, 40, 30)、D=(30, 30, 40)、E=(40, 20, 40)、F=(50, 20, 30)

0)、で表される六角形の内部または線上の範囲の主組成に、添加物として $WO_3$ を主組成に対して1~10重量部添加した組成からなり、当該材料成分を、所望の組合せて混合、粉碎、成形、および焼成する各工程を含み、且つ、前記焼成工程を $1100^{\circ}C \sim 1200^{\circ}C$ の温度範囲で行うことを特徴とする誘電体磁器組成物の製造方法である。

【0018】また、前記材料成分のうち複合ペロブスカイトのBサイト成分(Mg, Nb, Ti, W)の一種以上の元素を含む材料成分を、混合し、熱処理して、複合酸化物を予め生成し、その後他の材料成分を加えて所望の最終組成とすることを特徴とする誘電体磁器組成物の製造方法である。

【0019】更に本発明は、鉛系複合ペロブスカイトを主成分とする磁器組成物において、ペロブスカイト結晶粒内の芯部と側部との間に構成元素WとNbの不均一分布(コア-シェル構造)を伴う誘電体磁器組成物である。

【0020】更に本発明は、鉛系複合ペロブスカイトを主成分とする磁器組成物において、ペロブスカイト結晶粒内の芯部と側部との間に構成元素の不均一分布があり、最大濃度と最小濃度の差が最大濃度の20%以上である誘電体磁器組成物である。

【0021】また好ましくは、前記ペロブスカイト結晶粒の結晶粒径が $0.5\mu m$ 以上、 $10\mu m$ 以下である鉛系複合ペロブスカイトを主成分とする誘電体磁器組成物である。

【0022】

【作用】鉛系複合ペロブスカイトを主成分とする誘電体磁器組成物において、ペロブスカイト結晶粒内の芯部と側部との間に元素分布の不均一構造(コア-シェル構造)を形成させることにより、誘電率を著しく低下させることなく、誘電率の温度特性を平坦化させることができる。

【0023】また、結晶粒径成長を抑制することにより絶縁抵抗の劣化を防止しうる。

【0024】

【発明の具体的構成】

【0025】

【組成】本発明は、鉛系複合ペロブスカイトを主成分とする誘電体磁器組成物において、誘電率を著しく低下させることなく、誘電率の温度特性を平坦化させることを特徴とする。

【0026】本発明で用いる誘電体磁器組成物の主組成としては下記のものが使用できる。

【0027】即ち、マグネシウムニオブ酸鉛、チタン酸鉛、マグネシウムタングステン酸鉛からなる組成物 $[Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3 - Pb(Mg_{1/2}W_{1/2})O_3]$ において、以下の組成点A=(50, 30, 20)、B=(40, 40, 20)、C=

(30, 40, 30)、D=(30, 30, 40)、E=(40, 20, 40)、F=(50, 20, 30)、で表される六角形の内部または線上の範囲を主組成とするもの(図1に表示の範囲)である。

【0028】Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>-Pb(Mg<sub>1/2</sub>W<sub>1/2</sub>)O<sub>3</sub>の組成系の場合は、上記組成範囲外であると温度依存性が著しく損なわれたり、また、誘電率が著しく減少したりするためである。

【0029】また、より好ましい組成範囲としては、(40, 30, 30)、(43, 27, 30)、(40, 27, 33)であらわされる三角系の内部の範囲である。

【0030】また、本発明においては、上記の主組成に対しWO<sub>3</sub>を過剰に添加することを特徴とする。このWO<sub>3</sub>の過剰添加により誘電体磁器組成物中に元素分布の不均一な構造(コアシェル構造)を実現すると考えられる。

【0031】WO<sub>3</sub>の添加量は、前記の主組成に対し1~10重量部の範囲とする。WO<sub>3</sub>の添加量が1重量部未満だと温度特性の平坦化が不十分となり、また、10%をこえると誘電率の著しい減少を招くためである。また、より好ましいWO<sub>3</sub>の添加量は2~5重量部の範囲である。

【0032】

【微細組織】本発明は、誘電体磁器組成物の微細構造に特徴を有する。チタン酸バリウム系磁器組成物では、コアシェル構造によって誘電率の温度特性の平坦化が実現されていることが知られているが、本発明の複合ペロブスカイト誘電体磁器組成物についてもこの構造が実現されていることがわかった。

【0033】前述の先行技術文献にもTiがMg, Nb, Wと分離することの指摘がなされたが、これらではX7RまたはB特性を満たす程の温度特性の平坦化は生じていなかった。

【0034】他方、本発明の磁器組成物においては、NbとWの間にも強い分離の傾向が認められ、ペロブスカイト結晶粒内の芯部と側部との間に構成元素WとNbの不均一分布が生じ、実質的にコアシェル構造が形成されていることがわかった。

【0035】更にこの場合に、誘電率を極度に損ねることなく、誘電率の温度特性の平坦化がなされることを発見した。このコアシェル状の濃淡は、後述の実施例より、温度特性の平坦化が行われる場合に限って確認され、チタン酸バリウムの場合と同様にコアシェル構造の実現によって、誘電率温度特性の平坦化が行われたものと解釈できる。

【0036】ここで、ペロブスカイト結晶粒内の芯部と側部との間に構成元素不均一分布は、最大濃度と最小濃度の差で表したとき最大濃度の20%以上であることが好ましい。上記のような濃度変化が認められる場合に、

特に温度特性の改善がみられた。また、より好ましくは40%以上、更に好ましくは50%以上の不均一分布があることが望ましい。尚、ここでの濃度分析は、EPMAによる元素分布状態の解析により調べることができる。

【0037】

【結晶粒径】また、本発明の誘電体磁器組成物においては、その結晶粒径が0.5μm~10μmの範囲であることが好ましく、0.8μm~5μmの範囲がより好ましい。

【0038】結晶粒成長は一般的に絶縁抵抗の劣化をとめない誘電体磁器組成物として好ましくなく、また、積層セラミックコンデンサに应用する場合、薄層化の障害となる為である。他方、結晶粒径が小さすぎる場合には誘電率の減少が生じる為である。

【0039】本発明の組成において、WO<sub>3</sub>の添加は粒成長を抑制する効果もあり、前記のコアシェル構造の生成と同時に結晶粒径を10μm以下に抑えることができる。

【0040】

【製造方法】本発明の誘電体磁器組成物は次のような工程を経て得られる。すなわち、酸化物等の形で出発原料を前記の組成範囲内の所望の組成に秤量し、ボールミル等で混合・粉碎した後、乾燥し、必要により溶媒やバインダ成分を加えた上で印刷法、ドクターブレード法、プレス法等により所望の形に成形し、焼成を行う。

【0041】この場合の焼成温度は、通常1100℃~1200℃、より好ましくは1130℃から1180℃の温度範囲で行う。この焼成温度より低い場合には温度特性の平坦化が進まず、また、この温度より高い場合には磁器組成物の溶融が始まり好ましくない為である。

【0042】また上記の製造方法において、出発原料を生調合し最終組成を合成することもできるが、より好ましくは、複合ペロブスカイトのBサイト成分(Mg, Nb, Ti, W)となるものの少なくとも1種を含んだ出発原料を先に熱処理し、複合酸化物の形に合成しておき、これに残りの原料(PbO等)を加えて最終組成物を合成することが望ましい。

【0043】これは、Bサイト成分の熱処理を先に行わないで、生調合で磁器組成物を作成した場合でも、温度特性の平坦化は図られるが、この場合には誘電率の減少が見られることがあるためである。

【0044】この誘電率の低下の原因は、Bサイト成分中のNbやMgの作用によるものと考えられる。生調合で行う場合には、組成中のNbとPbが反応して誘電率の低いPb<sub>3</sub>Nb<sub>4</sub>O<sub>13</sub>等のニオブ酸鉛を生成したり、混合・粉碎時に比重の軽いMgが均一分散されずに誘電率の低下を招くものと考えられる。

【0045】故に先に合成すべき複合化合物としては、少なくともNbを含むニオブ化合物、より好ましくはN

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bとMgを含む複合化合物であることが好ましい。尚、ここでの複合酸化物はBサイト成分の全てを含む必要は必ずしもなく、その一部の成分を含むものでも良い。

【0046】上記の複合酸化物の生成は、構成成分の内、Bサイト成分(Pb以外の成分)の少なくとも1種を含む出発原料を、所定量秤量し混合、粉碎を経て熱処理を加えることにより行うことができる。この熱処理の温度は、通常500°C~1200°C、好ましくは800°C近傍の温度範囲で行う。

【0047】

【実施例】出発原料にPbO、MgO、Nb<sub>2</sub>O<sub>5</sub>、TiO<sub>2</sub>、WO<sub>3</sub>を用いた。各々の酸化物についてPbO、過剰のWO<sub>3</sub>に対応する分をのぞいた分(Bサイト相当分)を秤量の後、ジルコニアボールとともに24時間純水中で粉碎混合を行った。

【0048】乾燥の後1000°C、2時間の熱処理を施し中間組成物を得た。中間組成物を再度ジルコニアボールとともに24時間純水中で粉碎混合を行い乾燥を経て粉体とした。得られた粉体に所定量のPbOと過剰分のWO<sub>3</sub>を秤量、添加し同様にジルコニアボールとともに24時間純水中で粉碎混合を行った。乾燥後800°C2時間の条件で仮焼し、同様の粉碎、乾燥を経て目的の組成の粉体を得た。

【0049】この粉体にPVAを添加しプレス成形を施し、後記の表1~表3に記載した焼成温度にて焼結させ磁器組成物を得た。得られた磁器組成物に600°Cで銀電極を焼き付け試料とした。試料は円盤状で電極直径は8.5mm、電極間距離は0.7mm~1.5mmで、誘電特性の評価はインピーダンスアナライザ、絶縁抵抗は超絶縁抵抗計、粒径評価は走査型顕微鏡を用いた破断面の観察によってそれぞれ行った。比誘電率の温度変化率は20°Cの誘電率からの偏差(%)で示した。

【0050】後記の表1~表3より明らかなように、発明範囲外の組成では誘電率の温度特性が著しく劣ることがわかる。また、WO<sub>3</sub>を添加しない場合には温度特性が劣るほかに粒径が大きくなり、また、絶縁抵抗が低下する。WO<sub>3</sub>を15%添加した場合には誘電率の著しい低下が起こる。これらよりWO<sub>3</sub>の添加量は1ないし1

0%、好ましくは2ないし5%であることがわかる。

【0051】焼成温度については温度が高ければ高いほど温度特性の平坦化の傾向があるが1200°Cで一部の組成に溶融の兆候が見られる。このことを考慮すると焼成温度は1100°Cないし1200°Cが好ましいと思われる。

【0052】図2および図3に示す写真は、組成比(43、27、30)にWO<sub>3</sub>をそれぞれ5%、2%添加し1150°Cで焼成した場合の組成像であるが、コアシェル状に濃淡が現れている。このコアシェル状の濃淡は温度特性の平坦化が行われる場合に限って確認され、チタン酸バリウムの場合と同様にコアシェル構造の実現によって温度特性の平坦化が行われたと解釈できる。

【0053】図4および図5にこれら試料についてEPMAによって定量分析を行った結果を示す。図4は、組成比(43、27、30)にWO<sub>3</sub>を5%添加し1150°Cで焼成したものであり、図5は、同じ主組成にWO<sub>3</sub>を2%添加し1150°Cで焼成したものである。

【0054】各々の場合コアシェル状にW、Nb、Tiで濃度分布のあることがわかった。言い替えばNbとTiが集まり、Wがこれらと分離する事になる。

【0055】また、試料によってコア部とシェル部で構成元素比が逆転することも観察された。即ち、WO<sub>3</sub>=5%添加の図4の例では、ペロブスカイト結晶粒の中心部でWの濃度が高くなり、Ti、Nbの濃度が減少している。他方、WO<sub>3</sub>=2%添加の図5の例では、逆に結晶粒の中心部でTi、Nbの濃度が高くなり、Wの濃度が減少している。

【0056】図に示した組成物の場合、Wについてコア部とシェル部で20ないし50%以上の濃度変化が認められた。また、著しく温度特性の改善の見られない試料については濃度の変化は有意差が認められるほどには観測されなかった。したがって、著しく温度特性の改善されるためには構成元素の間でコア部とシェル部で20%以上、好ましくは40%以上、更に好ましくは50%以上の不均一分布があることが望ましい。

【0057】

【表1】

番号	組成比 PMN-PT-PbW	W03添加量 (重量部)	焼成温度 ℃	誘電率 偏差 %	抵抗率 log $\rho$	粒径 $\mu$ m
1	50-30-20	2	1150	7500 +5 -20	12.3	4.0
2		5	1150	5400 +2 -18	12.5	4.5
3	40-40-20	2	1150	6500 +10 -16	12.5	4.0
4		5	1150	4500 +15 -20	12.6	3.5
5	30-40-30	2	1150	6800 +10 -15	12.8	3.5
6		5	1150	5500 +2 -14	12.9	3.5
7	30-30-40	2	1150	6300 +3 -11	12.5	3.0
8		5	1150	3900 +2 -7	12.5	3.5
9	40-20-40	2	1150	6300 +4 -13	12.2	3.0
10		5	1150	4000 +3 -8	12.2	3.0
11	50-20-30	2	1150	7000 +3 -15	12.0	4.5
12		5	1150	5000 +5 -12	12.0	4.0

【0058】

【表2】

番号	組成比 PMN-PT-PMW	W03添加量 (重量部)	焼成温度 ℃	誘電率 偏差 %	抵抗率 log ρ	粒径 μm
13*	40-30-30	0	1150	15000 +20 -50	10.5	20
14		1	1150	9500 +5 -15	12.5	7.0
15		2	1150	9100 +5 -13	12.4	4.5
16		3	1000	12000 +10 -20	12.5	3.0
17		3	1100	8000 +3 -12	12.5	3.0
18		3	1150	6000 +2 -12	12.0	2.5
19		5	1200	4000 +1 -7	12.0	2.5
20		10	1150	4100 +3 -5	12.5	2.5
21*		15	1150	300 +2 -5	13.0	2.5
22*	43-27-30	0	1150	14000 +3 -45	10.2	25
23		1	1150	10500 +3 -20	12.1	8.0
24		2	1150	8400 +5 -12	12.0	5.0
25		3	1150	8100 +2 -9	12.4	4.0
26		5	1150	5100 +2 -7	12.9	2.0
27		10	1150	4200 +0 -5	12.3	2.5
27*		15	1150	500 +0 -5	13.5	2.5
29	43-30-27	2	1200	6500 +3 -9	12.5	3.5
30		3	1200	6000 +0 -7	12.5	3.5

【0059】

【表3】



番号	組成比 PMN-PT-PMW	VO <sub>3</sub> 添加量 (重量部)	焼成温度 ℃	誘電率 偏差 %	抵抗率 log ρ	粒径 μm
31*	53-27-20	5	1200	18000 +30 -55	12.3	5.0
32*		10	1150	3000 +20 -35	12.5	6.5
33*	45-40-15	5	1150	6000 +90 -20	12.3	4.0
34*		10	1150	4500 +80 -30	12.5	4.5
35*	30-45-25	2	1200	4500 +110 -20	12.5	5.5
36*		3	1200	3200 +90 -30	12.6	10
37*	25-35-40	2	1200	熔融		
38*		3	1200	熔融		

PMN-PT-PMWは $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3-Pb(Mg_{1/2}W_{1/2})O_3$ を示す。

#### 【0060】

【発明の効果】本発明によれば誘電率を著しく低下させることなく、温度による誘電率の変化を著しく小さく抑えることができる。また、鉛系複合ペロブスカイト系材料の特徴である低温焼成により安価な内部電極を使用することができ、バイアス電界によっても誘電率の低下の少ない積層セラミックコンデンサの誘電体として優れた磁器組成物を得ることができる。

#### 【0061】

【図面の簡単な説明】

図1は、本発明の主組成を示す3元組成図。図2は、本発明のペロブスカイト結晶粒のコアーシェル構造をしめす走査顕微鏡写真(WO<sub>3</sub> = 5%添加組成)。図3は、本発明のペロブスカイト結晶粒のコアーシェル構造をしめす走査顕微鏡写真(WO<sub>3</sub> = 3%添加組成)。図4は、本発明のコアーシェル構造部元素分布状態を示すのEPMAグラフ(WO<sub>3</sub> = 5%添加組成)。図5は、本発明のコアーシェル構造部元素分布状態を示すのEPMAGラフ(WO<sub>3</sub> = 3%添加組成)。

【図1】

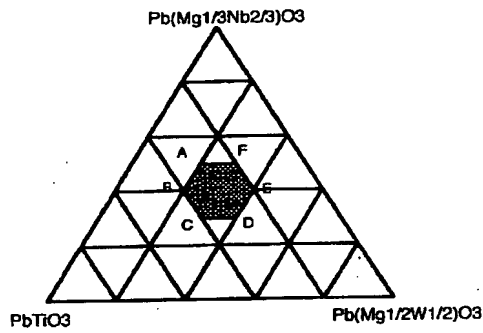
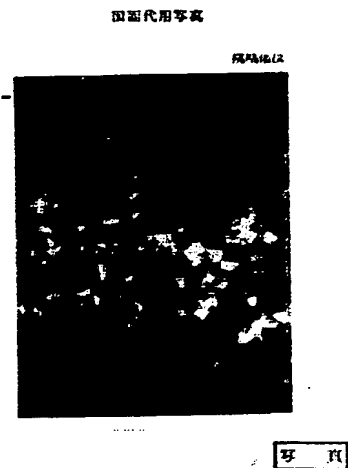
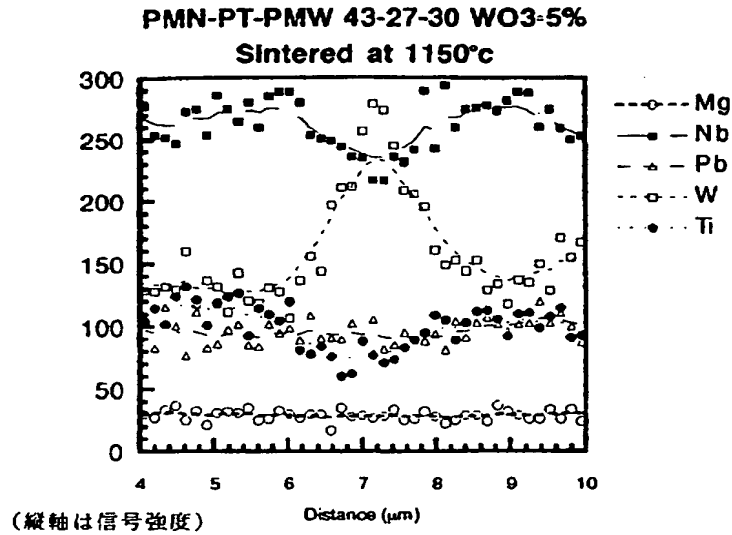


図1 本発明の主組成を示す3元組成図。

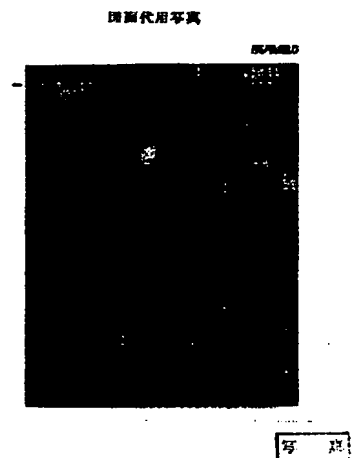
【図2】

図2 ペロブスカイト結晶粒のコアーシェル構造を  
しめす走査電鏡写真 (WO<sub>3</sub> = 5%添加組成)

【図4】

図4 コアーシェル構造部の元素分布状態を示す  
EPMAグラフ (WO<sub>3</sub> = 5%添加組成)

【図3】

図3 ペロブスカイト結晶粒のコアーシェル構造を  
しめす走査電鏡写真 (WO<sub>3</sub> = 2%添加組成)

【図5】

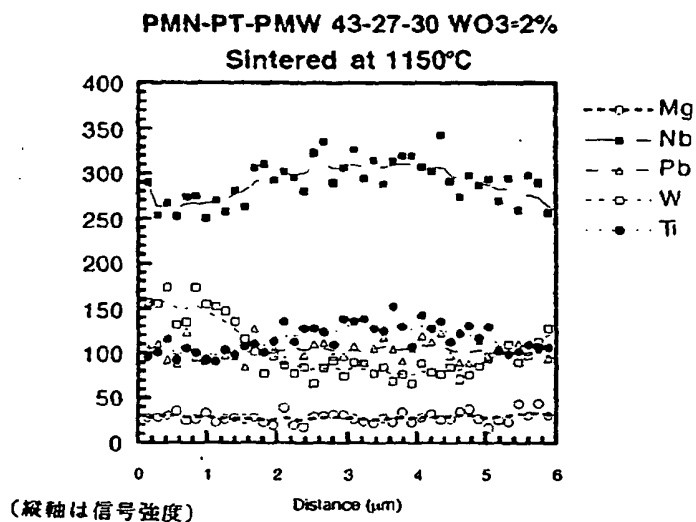


図5 コア-シェル構造部の元素分布状態を示す  
EDS線分析グラフ (WO<sub>3</sub> = 2%添加組成)

フロントページの続き

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(71)Applicant : TDK CORP

(22)Date of filing : 14.04.1992

(72)Inventor : UCHIKOBA FUMIO  
SAWAMURA KENTARO

## (54) DIELECTRIC PORCELAIN COMPOSITION AND MANUFACTURE THEREOF

## (57)Abstract:

PURPOSE: To significantly reduce change in the dielectric constant of a lead- combined perovskite dielectric material due to temperature without significantly lowering the dielectric constant.

CONSTITUTION: In a lead-combined perovskite dielectric porcelain composition,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3\text{--Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ ,  $\text{WO}_3$  is added by 1 to 10 parts by weight as additive to the main composition with the ranges of composition points as follows: A=(50, 30, 20), B=(40, 40, 20), C=(30, 40, 30), D=(30, 30, 40), E=(40, 20, 40) and F=(50, 20, 30). A core-shell structure of W and Nb is formed within the perovskite crystal grain.

## LEGAL STATUS

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## CLAIMS

## [Claim(s)]

[Claim 1] In the constituent  $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3, \text{PbTiO}_3, \text{and Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3]$  which consists of magnesium niobic-acid lead, a lead titanate, and a magnesium lead wolframate The following forming point  $A = (50, 30, 20)$ ,  $B = (40, 40, 20)$ ,  $C = (30, 40, 30)$ ,  $D = (30, 30, 40)$ ,  $E = (40, 20, 40)$ , the main composition of the interior of  $F = (50, 20, 30)$  and the hexagon come out of and expressed, or the range on a line -- as an additive --  $\text{WO}_3$  Dielectric porcelain constituent characterized by carrying out 1-10 weight section addition to the main composition.

[Claim 2] The dielectric porcelain constituent according to claim 1 whose diameters of crystal grain of the aforementioned dielectric porcelain constituent are 0.5 micrometers or more and 10 micrometers or less.

[Claim 3] In the manufacture method of a dielectric porcelain constituent a material component Magnesium niobic-acid lead, In the constituent  $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3, \text{PbTiO}_3, \text{and Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3]$  which consists of a lead titanate and a magnesium lead wolframate The following forming point  $A = (50, 30, 20)$ ,  $B = (40, 40, 20)$ ,  $C = (30, 40, 30)$ ,  $D = (30, 30, 40)$ ,  $E = (40, 20, 40)$ , to the main composition of  $F = (50, 20, 30)$ , the interior of the hexagon come out of and expressed, or the range on a line It is  $\text{WO}_3$  as an additive. It consists of composition which carried out 1-10 weight section addition to the main composition. The manufacture method of the dielectric porcelain constituent characterized by performing the aforementioned baking process by the 1100 degrees C - 1200 degrees C temperature requirement, including each process which mixes, grinds, fabricates and calcinates the material component concerned in a desired combination.

[Claim 4] The manufacture method of the dielectric porcelain constituent according to claim 3 characterized by mixing and heat-treating the material component which contains the element more than a kind of B site component (Mg, Nb, Ti, W) of a compound perovskite among the aforementioned material components, generating a multiple oxide beforehand, adding an other-materials component after that, and considering as the desired last composition.

[Claim 5] The dielectric porcelain constituent on the porcelain constituent which makes a lead system compound perovskite a principal component, and accompanied by an uneven distribution of the composition elements W and Nb to between the core part in perovskite crystal grain, and flanks.

[Claim 6] The dielectric porcelain constituent whose difference of the maximum concentration and the minimum concentration an uneven distribution of a composition element is between the core part in perovskite crystal grain, and a flank in the porcelain constituent which makes a lead system compound perovskite a principal component, and is 20% or more of the maximum concentration.

[Claim 7] The dielectric porcelain constituent according to claim 5 or 6 whose diameters of crystal grain of the aforementioned perovskite crystal grain are 0.5 micrometers or more and 10 micrometers or less.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] About the dielectric porcelain constituent used for a stacked type ceramic condenser etc., especially the dielectric constant of this invention is large, it has little temperature dependence, and low-temperature baking is possible for it, and it relates to a dielectric porcelain constituent with a fine particle size.

[0002]

[Description of the Prior Art] As a dielectric used for a stacked type ceramic condenser, the barium-titanate system dielectric has been used conventionally. By combining with an additive etc., by equivalent for the F property of JIS (it is the capacity deflection +30 and less than [ -80% ] in -25-+85 degrees C of temperature requirements), this dielectric shows the property which was [ have / about 5000 dielectric constant ] excellent, and has been widely used as a dielectric of a ceramic condenser by equivalent for about 15000 dielectric constant and X7R property (capacity deflection is less than \*\*15% in -55-+125 degrees C of temperature requirements).

[0003] on the other hand -- the demand of the miniaturization high capacity as recent years and an element -- a basis -- a \*\*\*\* stacked type ceramic condenser -- lamination has progressed [ neighboring dielectric thickness ] to about several microns further

[0004] Correspondence is becoming difficult as it has the feature to which a dielectric constant falls and the demand of the formation of small high capacity of an element increases so that the electric field which are impressed in the case of a barium-titanate system material are strong.

[0005] The lead system compound perovskite system material other than a barium-titanate system material is known as a high dielectric constant system material. This material shows about 25000 dielectric constant by equivalent for the F property of JIS, and examination of utilization has been widely performed as an interesting material. However, the volatilization of lead whose material of this cannot take a mechanical strength poses a problem, and is also material with many troubles -- it is easy to start insulation deterioration with plating liquid with difficult baking.

[0006] however, 1 micro F or more which needs many internal electrodes with a high dielectric constant since advantages, like having a high dielectric constant and it can generally calcinate at 1000 to about 1200 degrees C are got and the internal electrode of a stacked type ceramic condenser can be replaced with a palladium-silver alloy and 100% of silver from the conventional palladium 100% -- it has been comparatively put in practical use with the element of high capacity

[0007] Moreover, generally, reduction of the dielectric constant by bias electric field is small, and a lead system compound perovskite system material is an abbreviation half grade compared with a barium-titanate system material. Lead system compound perovskite system material has attracted attention also as a material corresponding to the demand to formation of small high capacity which was mentioned above.

[0008] A barium titanate shows phase transition serially, phase transition occurs near -10 degree C and near +120 degree C, and the peak of a dielectric constant also has the maximal value twice near [ this ] temperature corresponding to this.

[0009] Material with little temperature dependence, such as X7R property and B weighting (capacity deflection is less than \*\*10% in -25-+85 degrees C of temperature requirements), shows the with a dielectric constant of about 5000 property by combining composition uneven structures, such as an additive and core-shell structure, suitably for this.

[0010] On the other hand, in order that in the case of lead system compound perovskite system material phase transition generally might not be shown serially but the peak of a dielectric constant might also only show 1 time of the maximal value, unlike the barium-titanate system material, it was thought that it was difficult to show the property of the high dielectric constant in X7R property and B weighting.

[0011] In addition, about core-shell structure, although the Ceramic Society of Japan 1991 annual-convention lecture

\*\*\*\* collection 2 4th study group data 2 will have a report C34, pp266, and the JEOL Semiconductor Equipment & Materials International new functional compound electronic material study group in the Heisei 3 fiscal year, flattening of the temperature characteristic to the extent that X7R or B weighting is filled is not performed, and the publication about a dielectric constant is not seen, either.

[0012] The porcelain constituent having the advantage of this material and the temperature characteristic of a dielectric constant being flat about such a situation to a lead system compound perovskite system dielectric, and a dielectric constant being large is called for.

[0013]

[Problem(s) to be Solved by the Invention] When it was going to obtain a dielectric porcelain constituent with few rates of a temperature change using a  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$ - $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$  lead system compound perovskite system material, there was a problem that a dielectric constant generally decreased to 2000 to about 3000.

[0014] this invention is  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$ - $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ . It aims at not spoiling a dielectric constant remarkably using a lead system compound perovskite system material, and offering the dielectric porcelain constituent with few rates of a temperature change which doubles and has the advantage of a lead system compound perovskite system material.

[0015]

[Means for Solving the Problem] Namely, this invention is set to the constituent [ $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $\text{PbTiO}_3$ , and  $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ ] which consists of magnesium niobic-acid lead, a lead titanate, and a magnesium lead wolframate. The following forming point A= (50, 30, 20), B= (40, 40, 20), C= (30, 40, 30), D= (30, 30, 40), E= (40, 20, 40), the main composition of the interior of F= (50, 20, 30) and the hexagon come out of and expressed, or the range on a line -- as an additive --  $\text{WO}_3$  It is the dielectric porcelain constituent characterized by carrying out 1-10 weight section addition to the main composition.

[0016] Moreover, the diameter of crystal grain of the aforementioned dielectric porcelain constituent is the dielectric porcelain constituent which are 0.5 micrometers or more and 10 micrometers or less preferably.

[0017] this invention is set to the manufacture method of a dielectric porcelain constituent. a material component Moreover, magnesium niobic-acid lead, In the constituent [ $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $\text{PbTiO}_3$ , and  $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ ] which consists of a lead titanate and a magnesium lead wolframate The following forming point A= (50, 30, 20), B= (40, 40, 20), C= (30, 40, 30), D= (30, 30, 40), E= (40, 20, 40), to the main composition of F= (50, 20, 30), the interior of the hexagon come out of and expressed, or the range on a line It is  $\text{WO}_3$  as an additive. It consists of composition which carried out 1-10 weight section addition to the main composition. It is the manufacture method of the dielectric porcelain constituent characterized by performing the aforementioned baking process by the 1100 degrees C - 1200 degrees C temperature requirement, including each process which mixes, grinds, fabricates and calcinates the material component concerned in a desired combination.

[0018] Moreover, it is the manufacture method of the dielectric porcelain constituent characterized by mixing and heat-treating the material component which contains the element more than a kind of B site component (Mg, Nb, Ti, W) of a compound perovskite among the aforementioned material components, generating a multiple oxide beforehand, adding an other-materials component after that, and considering as the desired last composition.

[0019] Furthermore, this invention is a dielectric porcelain constituent accompanied by an uneven distribution (core-shell structure) of the composition elements W and Nb to between the core part in perovskite crystal grain, and flanks in the porcelain constituent which makes a lead system compound perovskite a principal component.

[0020] Furthermore, in the porcelain constituent which makes a lead system compound perovskite a principal component, this invention has an uneven distribution of a composition element between the core part in perovskite crystal grain, and a flank, and is a dielectric porcelain constituent whose difference of the maximum concentration and the minimum concentration is 20% or more of the maximum concentration.

[0021] Moreover, it is the dielectric porcelain constituent which makes a principal component preferably the lead system compound perovskite whose diameters of crystal grain of the aforementioned perovskite crystal grain are 0.5 micrometers or more and 10 micrometers or less.

[0022]

[Function] In the dielectric porcelain constituent which makes a lead system compound perovskite a principal component, flattening of the temperature characteristic of a dielectric constant can be carried out, without reducing a dielectric constant remarkably by making the uneven structure (core-shell structure) of an element distribution form between the core part in perovskite crystal grain, and a flank.

[0023] Moreover, degradation of insulation resistance can be prevented by suppressing the diameter growth of crystal grain.

[0024]

## [Elements of the Invention]

[0025]

[Composition] this invention is characterized by carrying out flattening of the temperature characteristic of a dielectric constant in the dielectric porcelain constituent which makes a lead system compound perovskite a principal component, without reducing a dielectric constant remarkably.

[0026] The following can be used as main composition of the dielectric porcelain constituent used by this invention.

[0027] Namely, it sets to the constituent  $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{-Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3]$  which consists of magnesium niobic-acid lead, a lead titanate, and a magnesium lead wolframate. The following forming point A= (50, 30, 20), B= (40, 40, 20), C= (30, 40, 30), D= (30, 30, 40), E= (40, 20, 40), F= (50, 20, 30), the interior of the hexagon come out of and expressed, or the range on a line is considered as the main composition

[0028] the case of the composition system of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{-Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$  -- the above-mentioned composition -- it is to spoil temperature dependence remarkably as it is out of range, and for a dielectric constant to decrease remarkably

[0029] Moreover, as a more desirable composition range, it is the range inside a triangular system expressed with (40, 30, 30), (43, 27, 30), and (40, 27, 33).

[0030] Moreover, it sets to this invention and is  $\text{WO}_3$  to the above-mentioned main composition. It is characterized by adding superfluously. This  $\text{WO}_3$  It is thought that superfluous addition realizes uneven structure (core-shell structure) of an element distribution in a dielectric porcelain constituent.

[0031]  $\text{WO}_3$  Let an addition be the range of 1 - 10 weight section to the aforementioned main composition. When flattening of the temperature characteristic will become inadequate if the addition of  $\text{WO}_3$  is under 1 weight section, and 10% is surpassed, it is for causing a remarkable reduction of a dielectric constant. Moreover, more desirable  $\text{WO}_3$  An addition is the range of 2 - 5 weight section.

[0032]

[Detailed organization] this invention has the feature in the fine structure of a dielectric porcelain constituent. Although it was known for the barium-titanate system porcelain constituent that flattening of the temperature characteristic of a dielectric constant is realized according to core-shell structure, it turns out that this structure is realized also about the compound perovskite dielectric porcelain constituent of this invention.

[0033] Flattening of the temperature characteristic to the extent that how to make indication of Ti separating also into the above-mentioned advanced-technology reference with Mg, Nb, and W fills X7R or B weighting with these was not produced.

[0034] On the other hand, in the porcelain constituent of this invention, it turns out that the inclination of separation strong also between Nb and W is accepted, an uneven distribution of the composition elements W and Nb arises, and core-shell structure is substantially formed between the core part in perovskite crystal grain, and a flank.

[0035] Furthermore, it discovered that did not spoil a dielectric constant in a degree very much in this case, and flattening of the temperature characteristic of a dielectric constant was made. The shade of the shape of this core shell is checked only within the case where flattening of the temperature characteristic is performed, from the below-mentioned example, and can be interpreted as that to which flattening of the dielectric constant temperature characteristic was performed by realization of core-shell structure like the case of a barium titanate.

[0036] Here, between the core part in perovskite crystal grain, and a flank, when the difference of the maximum concentration and the minimum concentration expresses, as for a composition element uneven distribution, it is desirable that it is 20% or more of the maximum concentration. When the above concentration change was accepted, especially the improvement of the temperature characteristic was found. Moreover, it is desirable for there to be 40% or more of 50% or more of uneven distributions still more preferably more preferably. In addition, the analysis of the element distribution state by EPMA can investigate concentration analysis here.

[0037]

[The diameter of crystal grain] Moreover, in the dielectric porcelain constituent of this invention, it is desirable that it is the range the diameter of crystal grain of whose is 0.5 micrometers - 10 micrometers, and the range which is 0.8 micrometers - 5 micrometers is more desirable.

[0038] A grain growth is because it becomes the obstacle of lamination, when it is not desirable as a dielectric porcelain constituent and generally applies to a stacked type ceramic condenser with degradation of insulation resistance. On the other hand, when the diameter of crystal grain is too small, it is for reduction in a dielectric constant to arise.

[0039] composition of this invention -- setting --  $\text{WO}_3$  Addition has the effect which suppresses grain growth and can hold down generation, simultaneously the diameter of crystal grain of the aforementioned core-shell structure to 10-micrometer less or equal.



[0040]

[The manufacture method] The dielectric porcelain constituent of this invention passes the following processes. Namely, after it carried out weighing capacity to composition of a request of a start raw material of aforementioned composition within the limits in the form of an oxide etc., and the ball mill etc. mixed and ground, and drying and adding a solvent and a binder component as occasion demands, it calcinates by fabricating in a desired form by print processes, the doctor blade method, the pressing method, etc.

[0041] 1100 degrees C - 1200 degrees C of burning temperature in this case are usually more preferably performed by the 1130 to 1180 degrees C temperature requirement. Flattening of the temperature characteristic does not progress to a low case from this burning temperature, and in being higher than this temperature, melting of a porcelain constituent starts, and it is because it is not desirable.

[0042] Moreover, more preferably, although a start raw material can be raw-prepared and the last composition can also be compounded in the above-mentioned manufacture method, although it becomes B site component (Mg, Nb, Ti, W) of a compound perovskite, it is desirable to heat-treat previously the start raw material containing at least one sort, to compound in the form of a multiple oxide, to add the remaining raw materials (PbO etc.) to this, and to compound the last constituent.

[0043] Although flattening of the temperature characteristic is attained even when a porcelain constituent is created by raw preparation without this heat-treating B site component previously, it is because reduction in a dielectric constant may be seen in this case.

[0044] It is thought that the cause of a fall of this dielectric constant is based on Nb in B site component or an operation of Mg. When carrying out by raw preparation, Nb and Pb under composition react and it is thought that the niobic-acid lead of the low Pb<sub>3</sub> Nb<sub>4</sub> O<sub>13</sub> grade of a dielectric constant is generated, or decline in a dielectric constant is caused, without carrying out uniform distribution of Mg with light specific gravity at the time of mixture and trituration.

[0045] Therefore, it is desirable that they are the niobium compound which contains Nb at least, and the conjugated compound which contains Nb and Mg more preferably as a conjugated compound which should be compounded first. In addition, there is not necessarily no need that a multiple oxide here contains all the B site components, and it may contain some of the components.

[0046] Generation of the above-mentioned multiple oxide can be performed by carrying out specified quantity weighing capacity of the start raw material containing at least one sort of B site component (components other than Pb) in a constituent, and adding heat treatment through mixture and trituration. the temperature of this heat treatment -- usually -- 500degreeC-1200degreeC -- it carries out by the temperature requirement near the 800 degreeC preferably

[0047]

[Example] It is PbO, MgO, Nb<sub>2</sub>O<sub>5</sub>, TiO, and WO<sub>3</sub> to a start raw material. It used. They are PbO and superfluous WO<sub>3</sub> about each oxide. Trituration mixture was performed for the part (an equivalent for B site) except the corresponding part in 24-hour pure water with the zirconia ball after weighing capacity.

[0048] 1000 degrees C and heat treatment of 2 hours were performed after dryness, and the middle constituent was obtained. Again, with the zirconia ball, trituration mixture was performed in 24-hour pure water, and the middle constituent was made into fine particles through dryness. as superfluous to the obtained fine particles as PbO of the specified quantity -- a part -- WO<sub>3</sub> weighing capacity -- it added and trituration mixture was similarly performed in 24-hour pure water with the zirconia ball Temporary quenching was carried out on 800-degree-C conditions of 2 hours after dryness, and the fine particles of the target composition were obtained through the same trituration and dryness.

[0049] Added PVA to these fine particles, performed press forming, it was made to sinter with the burning temperature indicated to after-mentioned Table 1 - 3, and the porcelain constituent was obtained. A silver electrode is burned at 600 degrees C to the obtained porcelain constituent. It considered as the attachment sample. A sample is [ 8.5mm and the inter-electrode distance of an electrode diameter ] 0.7mm - 1.5mm in the shape of a disk, and observation of the fracture surface where, as for a transcendence marginal ohm-meter and particle-size evaluation, evaluation of dielectric characteristics used the impedance analyzer, and insulation resistance used the scanned type microscope performed, respectively. The deflection (%) from the dielectric constant of 20 degrees C showed the rate of a temperature change of specific inductive capacity.

[0050] In the composition besides the invention range, it turns out that the temperature characteristic of a dielectric constant is remarkably inferior so that more clearly than after-mentioned Table 1 - 3. Moreover, WO<sub>3</sub> In not adding, the temperature characteristic is inferior, and also particle size becomes large, and insulation resistance falls. WO<sub>3</sub> When it adds 15%, the remarkable decline in a dielectric constant takes place. It is WO<sub>3</sub> from these. As for an addition, it turns out 1 or that it is 2 or 5% preferably 10%.

[0051] Although there is an inclination of flattening of the temperature characteristic the more the more temperature is

high about burning temperature, the signs of melting are looked at by a part of composition at 1200 degrees C. It is thought with taking this into consideration that 1100 degrees C or 1200 degrees C of burning temperature are desirable.

[0052] The photograph shown in drawing 2 and drawing 3 is WO<sub>3</sub> to a composition ratio (43, 27, 30). 5%, although it is a composition image at the time of adding 2% and calcinating at 1150 degrees C, the shade has appeared in the shape of a core shell, respectively. The shade of the shape of this core shell is checked only within the case where flattening of the temperature characteristic is performed, and can be interpreted as flattening of the temperature characteristic having been performed by realization of core-shell structure like the case of a barium titanate.

[0053] The result which carried out quantitative analysis to drawing 4 and drawing 5 by EPMA about these samples is shown. Drawing 4 is WO<sub>3</sub> to a composition ratio (43, 27, 30). It adds 5%, and calcinates at 1150 degrees C, and drawing 5 is WO<sub>3</sub> to the same main composition. It adds 2% and calcinates at 1150 degrees C.

[0054] It turns out that the shape of a core shell has a concentration distribution by W, Nb, and Ti in each case. In other words, Nb and Ti will gather and W will dissociate with these.

[0055] Moreover, it was also observed that a composition element ratio is reversed in the core section and the shell section by the sample. That is, in the example of drawing 4 of 3 = 5% addition of WO(s), the concentration of W becomes high in the core of perovskite crystal grain, and the concentration of Ti and Nb is decreasing. On the other hand, in the example of drawing 5 of 3 = 2% addition of WO(s), the concentration of Ti and Nb becomes high conversely in the core of crystal grain, and the concentration of W is decreasing.

[0056] In the case of the constituent shown in drawing, 20 or 50% or more of concentration change was accepted in the core section and the shell section about W. Moreover, about the sample as which the improvement of the temperature characteristic is not regarded remarkably, change of concentration was not observed at the forge fire a significant difference is accepted to be. Therefore, in order to improve the temperature characteristic remarkably, it is desirable for there to be 40% or more of 50% or more of uneven distributions still more preferably preferably 20% or more in the core section and the shell section between composition elements.

[0057]

[Table 1]

番号	組成比 PMN-PT-PKW	W03添加量 (重量部)	焼成温度 ℃	誘電率 偏差 %	抵抗率 log ρ	粒径 μm
1	50-30-20	2	1150	7500 +5 -20	12.3	4.0
2		5	1150	5400 +2 -18	12.5	4.5
3	40-40-20	2	1150	6500 +10 -16	12.5	4.0
4		5	1150	4500 +15 -20	12.6	3.5
5	30-40-30	2	1150	6800 +10 -15	12.8	3.5
6		5	1150	5500 +2 -14	12.9	3.5
7	30-30-40	2	1150	6300 +3 -11	12.5	3.0
8		5	1150	3900 +2 -7	12.5	3.5
9	40-20-40	2	1150	6300 +4 -13	12.2	3.0
10		5	1150	4000 +3 -8	12.2	3.0
11	50-20-30	2	1150	7000 +3 -15	12.0	4.5
12		5	1150	5000 +5 -12	12.0	4.0

[0058]

[Table 2]

番号	組成比 PMN-PT-PMW	W03添加量 (重量部)	焼成温度 ℃	跳電率 偏差 %	抵抗率 log ρ	粒径 μm
13*	40-30-30	0	1150	15000 +20 -50	10.5	20
14		1	1150	9500 +5 -15	12.5	7.0
15		2	1150	9100 +5 -13	12.4	4.5
16		3	1000	12000 +10 -20	12.5	3.0
17		3	1100	8000 +3 -12	12.5	3.0
18		3	1150	6000 +2 -12	12.0	2.5
19		5	1200	4000 +1 -7	12.0	2.5
20		10	1150	4100 +3 -5	12.5	2.5
21*		15	1150	300 +2 -5	13.0	2.5
22*	43-27-30	0	1150	14000 +3 -45	10.2	25
23		1	1150	10500 +3 -20	12.1	8.0
24		2	1150	8400 +5 -12	12.0	5.0
25		3	1150	8100 +2 -9	12.4	4.0
26		5	1150	5100 +2 -7	12.9	2.0
27		10	1150	4200 +0 -5	12.3	2.5
27*		15	1150	500 +0 -5	13.5	2.5
29	43-30-27	2	1200	6500 +3 -9	12.5	3.5
30		3	1200	6000 +0 -7	12.5	3.5

[0059]

[Table 3]

番号	組成比 PMN-PT-PMW	VO3添加量 (重量部)	焼成温度 ℃	誘電率 偏差 %	抵抗率 log ρ	粒径 μm
31*	53-27-20	5	1200	18000 +30 -55	12.3	5.0
32*		10	1150	3000 +20 -35	12.5	6.5
33*	45-40-15	5	1150	6000 +90 -20	12.3	4.0
34*		10	1150	4500 +80 -30	12.5	4.5
35*	30-45-25	2	1200	4500 +110 -20	12.5	5.5
36*		3	1200	3200 +90 -30	12.6	10
37*	25-35-40	2	1200	溶解		
38*		3	1200	溶解		

PMN-PT-PMWはPb(Mg $\frac{1}{3}$ Nb $\frac{2}{3}$ )O<sub>3</sub>-PbTiO<sub>3</sub>-Pb(Mg $\frac{1}{2}$ W $\frac{1}{2}$ )O<sub>3</sub>を示す。

[0060]

[Effect of the Invention] According to this invention, a dielectric constant cannot be reduced remarkably and change of the dielectric constant by temperature can be suppressed remarkably small. Moreover, a cheap internal electrode can be used by low-temperature baking which is the feature of lead system compound perovskite system material, and the porcelain constituent which was excellent with bias electric field as a dielectric of a stacked type ceramic condenser with little decline in a dielectric constant can be obtained.

[0061]

[Translation done.]

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

[Drawing 1]

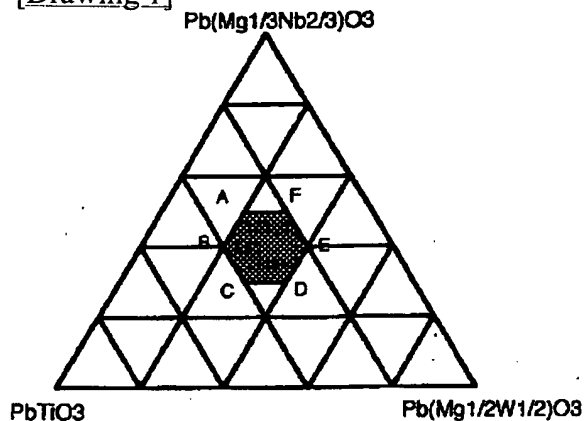


図1 本発明の主組成を示す3元組成図。

[Drawing 4]

**PMN-PT-PMW 43-27-30 WO<sub>3</sub>-5%**  
**Sintered at 1150°C**

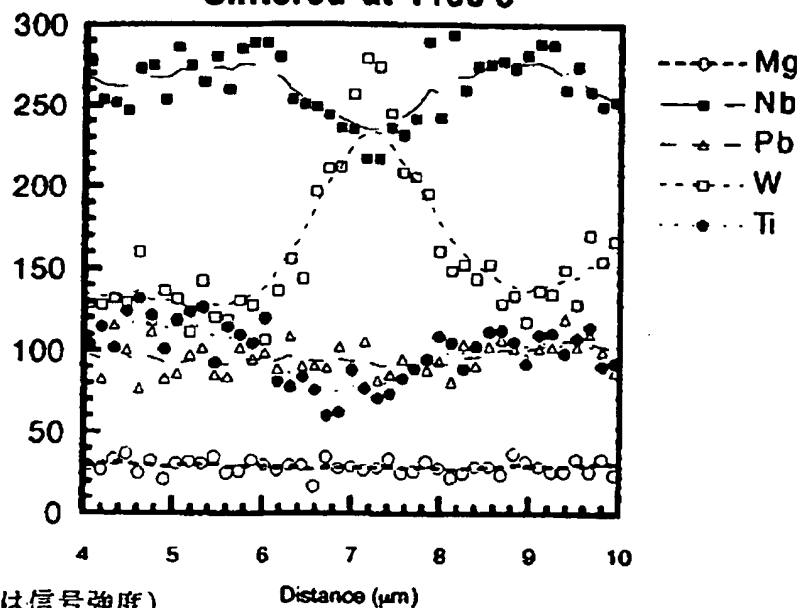


図4 コア-シェル構造部の元素分布状態を示す  
 EPMAグラフ (WO<sub>3</sub> = 5%添加組成)

[Drawing 2]

図面代用写真

図面代用写真



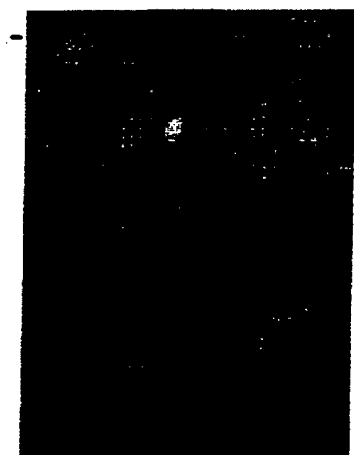
写真

図2 ペロブスカイト結晶粒のコア-シェル構造を  
しめす走査電鏡写真 (WO<sub>3</sub> = 5%添加組成)

[Drawing 3]

図面代用写真

図面代用写真



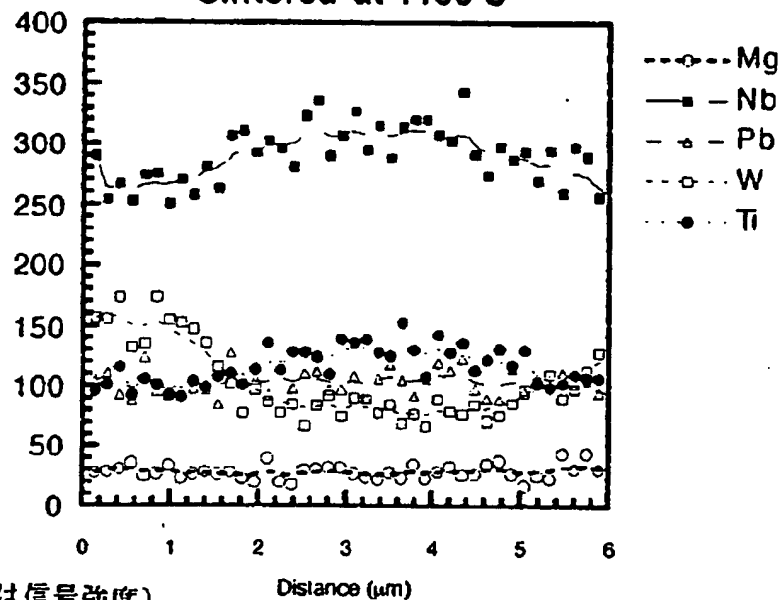
写真

図3 ペロブスカイト結晶粒のコア-シェル構造を  
しめす走査電鏡写真 (WO<sub>3</sub> = 2%添加組成)

[Drawing 5]

PMN-PT-PMW 43-27-30 WO<sub>3</sub>-2%

Sintered at 1150°C



(縦軸は信号強度)

図5 コア-シェル構造部の元素分布状態を示す

EPMAグラフ (WO<sub>3</sub> = 2% 添加組成)

[Translation done.]